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| <b>(54) Title:</b> GLASS-POLYALKENOATE CEMENTS<br><br><b>(57) Abstract</b><br><br>A dental cement made from poly(acrylic acid) and a zinc-containing glass such as $198\text{gZnO} + 138\text{gSiO}_2 + 32\text{gY}_2\text{O}_3$ combines the tolerance to dental pulp of zinc oxide-polycarboxylate dental cements with the adhesion to enamel and dentine of calcium-aluminosilicate-glass polyalkenoate cements.  |  |   |

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GLASS-POLYALKENOATE CEMENTS

This invention relates to a glass polyalkenoate cement, to a pack from which it can be made, and to a process for making it.

5 Zinc oxide based cements in the form of zinc eugenol, zinc phosphate and zinc polycarboxylate cements (described in British Patent 1139430) have all been used in dentistry for many years. The zinc component has a number of advantages - it is bland towards sensitive dental tissues, radio-opaque and is also  
10 thought to have an antibacterial effect.

Glass polyalkenoate cements have come into widespread use as a dental restorative material more recently, that is since the late 1970s, and have shown promise as a bone cement. Their  
15 adhesion to enamel and dentine was a major advance over previous dental restorative materials, with their acid-erosion resistance and their ability to exude fluoride being further advantages. Therefore they largely replaced zinc poly(carboxylate) cement, which had had the drawback of weakness which, it is now  
20 tentatively believed, was unavoidably inherent in the material due to the presence of surface pores acting as stress-raising flaws. Zinc carboxylate cements suffered a further drawback, namely indifferent appearance due to their porous surface finish and due to their opacity, contrasting with tooth translucency. These drawbacks further contributed to making glass polyalkenoate  
25 cements into the material of choice for anterior dental fillings.

Glass polyalkenoate cements, also known as glass ionomer cements, are formed by the reaction of a poly(carboxylic acid) and an ion-leachable glass. Such cements are described and claimed for example in British Patent No 1,316,129, in which the  
30 acid is poly(acrylic acid) and the glass is a calcium fluoroaluminosilicate glass powder. Similar cements for large volume application based on ion-leachable fluoroaluminosilicate glass of low fluorine content are described in British Patent, 1,532,954.

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In these (and earlier) silicate cements, cement formation depends on the acid degradability of the silicate. This acid degradability has in turn historically been studied in the context of aluminosilicate minerals, where it was found to be critically dependent on the Al:Si ratio. By-passing the weight of this evidence and the whole trend of the teaching in this art, it has now been found that high-zinc silicate glasses may be used to form polyalkenoate cements. These cements combine the desirable properties of the polycarboxylate cements based on zinc oxide described in British Patent 1,139,430, namely radio opacity, tolerance to dental pulp, early hydrolytic stability and ease of handling, with the advantages of calcium-aluminosilicate-glass polyalkenoate cements, namely low porosity, excellent surface finish and, of course, adhesion to enamel and dentine. Presentation of the zinc in vitreous form has turned out to offer a double advantage: (i) avoiding the use of crystalline or physically blended forms of zinc oxide has avoided harmful inhomogeneity in the cement, and (ii) zinc atoms in a glass are by definition not in their minimum-energy lattice positions, and are therefore energetically more encouraged to react with cement-forming acid than are zinc atoms in an oxide, salt or other crystalline form. This extra reactivity shortens the setting time of the cements. Certain of these cements are aluminium-free, and others are lower-aluminium than heretofore, when the Al:Si ratio had been thought to be all-important.

According to the present invention, there is provided a pack for making a cement, the pack comprising a water-soluble poly(carboxylic acid) or hydrolysable precursor thereof, and a silicate glass or a sol-gel precursor thereof containing at least 30 atom % zinc (not counting oxygen atoms nor any fluorine atoms in the glass).

A pack can take many different forms. For example, it may be a kit or box containing the specified components in separate containers, which may be relatively large (resealable) or

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disposable, containing the correct quantity for one treatment. The pack could alternatively comprise the components mixed in the appropriate proportions in a single container, as long as anhydrous conditions can be maintained until the time of use.

5 While, especially for in-vivo applications, it need not contain any at all, the glass may contain up to 20 atom % of trivalent cations (again, not counting oxygen atoms nor any fluorine atoms in the glass), such as aluminium, lanthanum or yttrium or any mixture thereof. Preferably the proportion does  
10 not exceed 6 atom %. It may be at least 3 atom %, e.g. 4 to 6%. The atomic ratio of silicon to trivalent cation may be (from 4 to 10):1, preferably (from 7 to 10):1, more preferably (from 8 to 10):1.

The glass may also contain divalent cations other than zinc,  
15 in an atomic proportion not exceeding one-third of the zinc, optionally not exceeding one-fifth, generally not exceeding one-tenth.

The glass preferably contains 25 to 50 atom % silicon (not counting oxygen atoms nor any fluorine atoms in the glass).

20 The invention also provides a process for the preparation of a glass polyalkenoate cement, which comprises mixing a water-soluble poly(carboxylic acid), or a hydrolysable precursor thereof, with a zinc-containing silicate glass as hereinbefore defined in the presence of water, and if desired a water-soluble  
25 chelating agent, in proportions and conditions to form a cement. The invention also provides a glass polyalkenoate cement itself, being the product of an acid and glass as defined, such cement being a new product in its own right.

In this specification the glass compositions are described in  
30 the conventional manner as containing silica, zinc oxide, alumina and other oxides though it is to be understood that these oxides are chemically combined in the zinc silicate, or zinc aluminosilicate glass and are not actually present as the free oxides.

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The proportions of oxides for the glass compositions refer to the amounts of these oxides (added in some cases as the corresponding carbonates) present in the glass frit. The glass composition may alternatively be arrived at using sol gel techniques.

5       The weight ratio of the acidic oxides (e.g.  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$  and  $\text{P}_2\text{O}_5$ ) to the basic oxides (i.e. all metal oxides) in the zinc silicate or zinc alumino silicate glass is usually chosen such that the polycarboxylate cement stiffens within a relatively short period, termed the working time, which is usually less than  
10       twenty-five minutes. It has been found that the rate of reaction increases with increasing basicity of the glass and thus the ratio of the oxides can be chosen in order to allow adequate working time to form the cement into the desired shape before it has set. For dental applications it is preferred to attain a  
15       working time of about five minutes or less and then have the shortest possible setting time in which the set cement hardens and attains an appreciable compressive strength. The ratio by weight of acidic to basic oxides in the glass may be from 0.1 to 3.0 and preferably from 0.2 to 2.5:1.

20       The principal acidic oxide in the glass is usually silica, although the glass may in addition contain minor amounts of boron oxide, or phosphorus pentoxide. The principal basic oxide in the glass is zinc oxide. Minor amounts of alumina may also be incorporated which although it has amphoteric properties can be  
25       considered as a basic oxide for the purposes of the present specification.

      The glass desirably contains at least one other oxide or fluoride in amounts totalling up to 50 weight %. Examples of such other basic oxides include alumina, zirconia, titania,  
30       calcium oxide, magnesium oxide, lanthanum oxide, barium oxide, strontium oxide, yttrium oxide, titanium oxide, zirconium oxide, lithium oxide, sodium oxide and potassium oxide, although alkali metal oxides may be undesirable for some applications because they impart increased solubility to the resulting cements.

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Examples of such other fluorides include stannous fluoride and cryolite, and fluorides of any of the above named metals, especially calcium fluoride and zinc fluoride. Fluoride has the advantage of reducing the viscosity of molten glass, and  
5 aluminium is desirably then present to limit the loss of fluorine via  $\text{SiF}_4$  in the gas phase. Preferred glasses for use in the present invention include those falling within the composition range 10 to 65 weight % silica, 15 to 65 weight % zinc oxide.

The zinc silicate or zinc alumino-silicate glasses used in  
10 the present invention may be prepared by fusing mixtures of the components in the appropriate proportions at temperatures above  $900^\circ\text{C}$  and preferably in the range  $1050^\circ\text{C}$  to  $1600^\circ\text{C}$ . The mixture is preferably fused for from 1 to 4 hours. Silica, zinc oxide and alumina may be included in the mixture as oxides, but it is  
15 often convenient to add other oxides as the carbonate, and references to the presence of oxides in the glass fusion mixture includes the possibility that they may be added as carbonates, or as other compounds which decompose similarly under glass fusion conditions to give the oxides.

20 The addition of carbonates to the fusion mixture lowers the fusion temperature and thus these can be considered as fluxing agents. If desired, however, the mixture may contain an additional fluxing agent, and this has been found to be important with glass compositions containing only silica, zinc oxide and  
25 alumina. In this connection fluorides such as zinc fluoride, fluorite, stannous fluoride and cryolite have been found useful as fluxing agents. Other fluxing agents, for example calcium phosphate and aluminium phosphate, may also be less preferably used. The total amount of fluxing agents present in the mixture,  
30 including carbonates, may be up to 50% but preferably not more than 15% by weight, based on the total weight of the mixture.

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After fusion the glass may be poured off and cooled rapidly, for example, in air or water or some combination of both. To a first approximation the proportions of the different elements in the glass may be taken as the proportions of the same elements present in the mixture. Some fluorine may, however, be lost from a fluoride fluxing agent during glass formation.

The glasses used in the present invention may be readily obtained in fine powder form. Sol gel techniques are especially appropriate for this. The degree of fineness of the powder should preferably be such that it produces a smooth cement paste which sets within an acceptable period when mixed with the poly(carboxylic acid) in the presence of water. Preferably the degree of fineness of the powder is such that it will pass through a 150 mesh B.S. sieve (0.1mm apertures) and most preferably such that it will pass through a 350 mesh B.S. sieve (0.04mm apertures). Mixtures of different glasses may be used if desired. The glass may be acid-washed or more preferably heat treated below the glass transition temperature, to improve the ratio (working time):(setting time).

The preferred poly(carboxylic acid)s are those prepared by the homopolymerisation and copolymerisation of unsaturated aliphatic carboxylic acids for example acrylic acid, itaconic acid, mesaconic acid, citraconic acid, maleic and aconitic acid, and copolymerisation of these acids with other unsaturated aliphatic monomers for example acrylamide and acrylonitrile. Particularly preferred are the homopolymers of acrylic acid, and copolymers thereof, in particular copolymers of acrylic acid and itaconic as described and claimed in British Patent No. 1,484,454. It is also possible to use a precursor of a poly(carboxylic acid) which will be transformed into the poly(carboxylic acid) on contact with water, for example a poly(carboxylic acid anhydride) or other suitable polymer. The poly(carboxylic acid anhydride) may be a homopolymer of an unsaturated carboxylic acid anhydride, or a copolymer with a



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vinyl monomer, and particularly a vinyl hydrocarbon monomer. Good results may be obtained using homopolymers of maleic anhydride and copolymers thereof with ethylene, propene, butene and styrene.

5       The poly(carboxylic acid) or precursor thereof is preferably linear although branched polymers may also be used, and preferably has an average molecular weight of from 1000 to 150,000 and most preferably from 5000 to 100,000. In this specification the average molecular weight is that measured by an  
10 absolute method such as light scattering, or ultracentrifuge sedimentation.

Cement packs in accordance with this invention preferably comprise the poly(carboxylic acid) in the form of an aqueous solution containing from 20 to 65% by weight of the  
15 poly(carboxylic acid). The cement pack may be a two-part pack in which the weight ratio of zinc silicate glass to liquid in the two parts is from 1.5:1 to 8:1 and preferably from 1.5:1 to 5.5:1, so that when the entire contents of the pack are mixed together a rapidly hardening cement is obtained. In another  
20 embodiment the pack may contain the glass and the liquid in separate capsules, the total amount of glass in the pack and the total amount of liquid in the pack being in the appropriate ratio. In a further embodiment, both components may be encapsulated in the same capsule in the desired ratio, provided  
25 that a user-rupturable barrier prevents premature reaction. In a still further embodiment the pack may comprise an intimate mixture of the zinc silicate glass and the poly(carboxylic acid) in anhydrous (e.g. freeze-dried) powder form, the total amount of the components in the mixture being in the appropriate ratio.  
30 Water may be included in the pack provided that the pack has means to prevent premature reaction. In the above-mentioned embodiments the glass is preferably from 15 to 85% by weight, the poly(carboxylic acid) is preferably from 3 to 50% by weight, and the water is preferably 5 to 70% by weight, based on the total  
35 weight of the components.

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- The poly(carboxylate) cements of this invention may be made up in the conventional manner. Thus the materials in the one or two-pack are brought together and mixed forming a plastic mass which can be cast, moulded, or otherwise formed in the required shape during the brief period in which the mixture retains its plastic properties. The components can be mixed quite rapidly to give a uniform mass which commences to harden in a few minutes and is usually set within twenty-five minutes of mixing. The rate of hardening and strength of the final product are partly determined by the glass-liquid ratio which for the highest ultimate strength is preferably as high as possible compatible with adequate working time. The optimum ratio for a particular zinc silicate glass and poly(carboxylic acid) may be determined readily with preliminary experiments. Too little or too much glass normally results in a mixture that is more difficult to form into a desired shape. Particularly good results have been obtained using the components in the ratio of 2 to 10 parts by weight of zinc silicate glass for each part by weight of the poly(carboxylic acid) or precursor thereof.
- The invention also provides a water hardenable cement composition which comprises an intimate mixture of a water soluble poly(carboxylic acid) or a hydrolysable precursor thereof, a water soluble chelating agent and a zinc silicate or zinc aluminosilicate glass as hereinbefore defined.
- The poly(carboxylate) cements of the present invention may find application in dentistry, and in orthopaedic surgery where they may be used to assist in the resetting of fractured bone material or as a bone substitute material or as bone cement. In addition the aluminium free glass composition of the present invention may find use as a cement matrix for the controlled delivery of drugs.

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The invention is illustrated by the following Examples:-

EXAMPLE 1.

A series of glasses I, II and III are prepared by fusing mixtures of silica, zinc oxide and alumina as set out in Table 1 below in a sillimanite crucible. After fusion the glass is poured off and cooled rapidly. The glass compositions and fusion conditions are as follows:-

TABLE 1.

|    |                                | <u>I</u> |      | <u>II</u> |      | <u>III</u> |     |
|----|--------------------------------|----------|------|-----------|------|------------|-----|
|    |                                | g        | mol  | g         | mol  | g          | mol |
| 10 |                                |          |      |           |      |            |     |
| 15 | SiO <sub>2</sub>               | 138      | 2.3  | 126       | 2.1  | 144        | 2.4 |
|    | ZnO                            | 198      | 2.44 | 215       | 2.64 | 170        | 2.1 |
|    | Al <sub>2</sub> O <sub>3</sub> | 26       | 0.5  | 26        | 0.5  | 51         | 1.0 |
| 20 | Fusion temperature (°C)        | 1550     |      | 1520      |      | 1550       |     |
|    | Time (hours)                   | 2        |      | 2         |      | 2          |     |

25

The resultant glasses are dried and crushed until they pass through a 350 mesh B.S. (0.04mm) sieve.

Cements are prepared by mixing the crushed glasses with a 47 weight % aqueous solution of polyacrylic acid of number average molecular weight  $M_u = 11000$  and weight average molecular weight  $M_w = 22700$ . The properties of the resulting cements are set out in Table 2:-

30

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TABLE 2

|  | <u>I</u> | <u>II</u> | <u>III</u> |
|--|----------|-----------|------------|
| 5 Working Time (minutes)   | 1.2      | 1.3       | 1.9        |
| Setting time in minutes as defined<br>by using an Oscillating Rheometer  | 10.1     | 5.7       | 16.4       |
| 10 Compressive strength developed<br>after 24 hrs in water at 37°C (MPa) | 57       | 93        | 43         |
| Powder/Liquid ratio (g/ml)   | 3:1      | 3:1       | 3:1        |
| 15 All the cements prepared are found to be hydrolytically stable.       |          |           |            |

EXAMPLE 2.

A series of glasses are prepared by fusing mixtures A-F of compounds in approximately 350g amounts in the molar proportions listed in Table 3. Fusion conditions are between 1400 and 1550°C for one to four hours. The resulting glasses are dried and crushed until they pass through a 350 mesh B.S. (0.04mm) sieve. Cements are prepared by mixing the crushed glasses with a 57 weight % aqueous solution of a polyacrylic acid of molecular weight as in Example 1. The properties of the cements are set out in Table 4.

5

TABLE 3  
GLASS COMPOSITIONS

|    | A                      |      | B                       |      | C                      |      | D                      |      | E                       |      | F                      |      |
|----|------------------------|------|-------------------------|------|------------------------|------|------------------------|------|-------------------------|------|------------------------|------|
|    | g                      | mol% | g                       | mol% | g                      | mol% | g                      | mol% | g                       | mol% | g                      | mol% |
| 10 | SiO <sub>2</sub> (138) | 46%  | SiO <sub>2</sub> (138)  | 46%  | SiO <sub>2</sub> (126) | 42%  | SiO <sub>2</sub> (138) | 46%  | SiO <sub>2</sub> (138)  | 46%  | SiO <sub>2</sub> (138) | 46%  |
| 15 | ZnO (198)              | 50%  | ZnO (178)               | 44%  | ZnO (215)              | 53%  | ZnO (198)              | 49%  | ZnO (198)               | 49%  | ZnO (198)              | 48%  |
| 20 | ZnF <sub>2</sub> (23)  | 4%   | AlO <sub>1.5</sub> (26) | 10%  | CaO (13)               | 5%   | CaF <sub>2</sub> (20)  | 5%   | LaO <sub>1.5</sub> (43) | 5%   | YO <sub>1.5</sub> (32) | 6%   |

20

TABLE 4  
CEMENT PROPERTIES

|                            | A   | B   | C    | D   | E   | F     |
|----------------------------|-----|-----|------|-----|-----|-------|
| Powder: Liquid             | 3:1 | 3:1 | 4:1  | 4:1 | 4:1 | 4.5:1 |
| Working Time (mins)        |     |     |      |     |     |       |
| Setting Time (mins)        | 16  | 1.8 | 11.6 | 8.8 | 3.6 | 2.2   |
| Compressive strength (MPa) | 31  | 60  | 63   | 64  | 77  | 91    |
| Flexural Strength (MPa)    | 8   | 12  | 14   | 14  | 8   | 13    |

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## EXAMPLE 3

Various samples of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-ZnO}$  glasses were made by the procedure described in Example 1, and were ground in a vibratory mill. A ball mill gave inferior (though still adequate) results.

- 5 The fraction smaller than 45 microns was heat treated in 35g batches for 3 hours at 650°C and furnace cooled. (The glass transition temperature of all the samples was in the range 700-704°C.)

Other samples were: untreated; were heat-treated and also acid-washed (in 50ml of 5% acetic acid, stirred for 1 hour, recovered under vacuum and dried in a convection oven); or were  
10 acid-washed without heat treatment. In general, however, the overall most convenient working times, setting times, and working/setting ratios were obtained using simply heat treated glass. This remained true even after trials of chelating agents  
15 such as tartaric acid and certain phosphonic acids, which were therefore not used in this Example.

The samples were made into cements using poly(acrylic acid) in a p/l ratio of 3:1 according to the procedure described in Example 1, and the results are tabulated in Table 4. All showed satisfactory  
20 water stability.

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TABLE 4 (Example 3)

| 5  | Example   | 3(i)                 | 3(ii)                | 3(iii)               |
|----|---|----------------------|----------------------|----------------------|
| 10 | $\text{SiO}_2$ )<br>$\text{Al}_2\text{O}_3$ )<br>$\text{ZnO}$ )<br>mole<br>fraction | 0.45<br>0.05<br>0.50 | 0.44<br>0.05<br>0.51 | 0.40<br>0.05<br>0.55 |
| 15 | Melt temp<br>Melt time  | 1550°C<br>2 hrs      | 1500°C<br>3 hrs      | 1550°C<br>2 hrs      |
| 20 | Working<br>time   | 1 min 36s            | 1 min 58s            | very short           |
| 20 | Setting<br>time   | 7 mins 45s           | 8 mins 54s           | very rapid           |
| 25 | Compressive<br>Strength (MPa)   | 80.4                 | 63.2                 | 62.7                 |

## EXAMPLE 4

30 A glass was made up by the procedure in Example 1, in this case having the composition (in mole ratios):

35 CaO 0.05  
ZnO 0.53  
SiO<sub>2</sub> 0.42

Various cements were made with this glass, using freeze-dried poly(acrylic acid).

40 The following results are given in terms of the powder:liquid ratio, which is the weight of glass powder to the weight of water, whilst the poly(acrylic acid) concentration is expressed as the weight of acid over the weight of water. It is worth commenting here that, because zinc has a much higher atomoc weight than calcium or aluminium, the zinc-oxide-based glasses are appreciably denser  
45 than conventional ionomer glasses and this explains the high powder:liquid ratios used.

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Compressive strengths were determined as in the preceding Examples. Flexural strengths were also determined, as follows. Flexural testpieces measuring approximately 3.0 x 3.0 x 25.0 mm were produced using split silicone coated stainless steel moulds. The cements, because of their low viscosity, flowed readily into the gap between the two halves of the mould, which resulted in a flash that broke off the specimen leaving edge flaws when demoulding. (These edge flaws are almost certainly substantially and artificially reducing the flexural strengths obtained.) The tests were carried out at room temperature and the flexural strengths and Young's moduli calculated.

Working times and setting times were also determined as in the preceding Examples. The results obtained for all these properties were as follows:

|    |                         |                           |                                  |                                |                             |              |
|----|-------------------------|---------------------------|----------------------------------|--------------------------------|-----------------------------|--------------|
| 15 |                         |                           |                                  |                                |                             |              |
|    | <u>Powder</u><br>Liquid | Acid<br>Concentration     | Compressive<br>Strength<br>(MPa) | Standard<br>Deviation<br>(n=5) |                             |              |
| 20 |                         |                           |                                  |                                |                             |              |
|    | 3:1                     | 45%                       | 38.61                            | 4.30                           |                             |              |
|    | 4:1                     | 53%                       | 54.43                            | 7.67                           |                             |              |
|    | 4:1                     | 57%                       | 62.74                            | 3.76                           |                             |              |
| 25 |                         |                           |                                  |                                |                             |              |
|    | <u>Powder</u><br>Liquid | Acid<br>Concentration     | Flexural<br>Strength<br>(MPa)    | S.D<br>(n=5)                   | Young's<br>Modulus<br>(GPa) | S.D<br>(n=5) |
| 30 |                         |                           |                                  |                                |                             |              |
|    | 4:1                     | 57%                       | 14.49                            | 1.57                           | 4.00                        | 12.18        |
| 35 |                         |                           |                                  |                                |                             |              |
|    | <u>Powder</u><br>Liquid | Polyacid<br>Concentration | Working<br>Time                  | Setting<br>Time                |                             |              |
| 40 |                         |                           |                                  |                                |                             |              |
|    | 3:1                     | 53%                       | 1min 33s                         | 13min 24s                      |                             |              |
|    | 4:1                     | 53%                       | 48s                              | 6min 24s                       |                             |              |
|    | 4:1                     | 57%                       | 1min 36s                         | 11min 36s                      |                             |              |



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CLAIMS

1. A pack for making a cement, the pack comprising a water-soluble poly(carboxylic acid) or hydrolysable precursor thereof, and a silicate glass (or a sol-gel precursor thereof) containing at least 30 atom % zinc not counting oxygen atoms nor any fluorine atoms in the glass.
2. A pack according to Claim 1, in which the silicate glass contains up to 20 atom % of trivalent cations on the same basis.
3. A pack according to Claim 2, in which the silicate glass contains up to 6 atom % of trivalent cations on the same basis.
4. A pack according to any preceding claim, in which the silicate glass contains at least 3 atom % of trivalent cations on the same basis.
5. A pack according to any preceding claim, in which the silicate glass contains trivalent cations in an atomic ratio silicon:trivalent cation of (4 to 10):1.
6. A pack according to Claim 5, wherein the said atomic ratio is (7 to 10):1.
7. A pack according to Claim 6, wherein the said atomic ratio is (8 to 10):1.
8. A pack according to any preceding claim, in which the silicate glass also contains divalent cations other than zinc, in an atom proportion not exceeding one-third of the zinc.
9. A pack according to Claim 8, wherein the said other divalent cations do not exceed one-fifth of the zinc.
10. A pack according to Claim 9, wherein the said other divalent cations do not exceed one-tenth of the zinc.
11. A pack according to any preceding claim, wherein the glass contains 25 to 50 atom % silicon not counting oxygen atoms nor any fluorine atoms in the glass.
12. A pack according to any preceding claim, wherein the silicate glass contains 10 to 65 weight % silica and 15 to 55 weight % zinc oxide.

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13. A process for the preparation of a glass polyalkenoate cement, which comprises mixing the components of a pack according to any preceding claim, in the presence of water.
14. A glass polyalkenoate cement which has been prepared by a process according to Claim 13.
15. A glass polyalkenoate cement in which the glass contains at least 30 atom % zinc not counting oxygen atoms nor any fluorine atoms in the glass.
16. A glass polyalkenoate cement according to Claim 15, wherein the glass is as set forth in any of Claims 2 to 12.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/00444

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|--|--|---|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>  |  |   |
| According to International Patent Classification (IPC) or to both National Classification and IPC  |  |   |
| Int.Cl. 5 A61K6/083;<br>A61L15/07  | C04B28/28;   | C03C4/00; A61L25/00   |
| <b>II. FIELDS SEARCHED</b>   |  |   |
| Minimum Documentation Searched <sup>7</sup>  |  |   |
| Classification System  | Classification Symbols   |   |
| Int.Cl. 5  | A61K ; C04B ; C03C ; A61L  |   |
| Documentation Searched other than Minimum Documentation<br>to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>  |  |   |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>  |  |   |
| Category <sup>10</sup>   | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup> | Relevant to Claim No. <sup>13</sup>                               |
| Y  | FR,A,2 370 468 (ICI)<br>9 June 1978<br>see page 4, line 17 - line 32; claims<br>---                            | 1-16  |
| Y  | WO,A,8 200 827 (MINNESOTA MINING AND<br>MANUFACTURING COMPANY)<br>18 March 1982<br>see claims<br>---           | 1-16  |
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| <sup>10</sup> Special categories of cited documents :<br>"A" document defining the general state of the art which is not considered to be of particular relevance<br>"E" earlier document but published on or after the international filing date<br>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)<br>"O" document referring to an oral disclosure, use, exhibition or other means<br>"P" document published prior to the international filing date but later than the priority date claimed<br>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention<br>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step<br>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.<br>"A" document member of the same patent family |  |   |
| <b>IV. CERTIFICATION</b>   |  |   |
| Date of the Actual Completion of the International Search<br>02 JUNE 1993  |  | Date of Mailing of this International Search Report<br>16. 06. 93 |
| International Searching Authority<br>EUROPEAN PATENT OFFICE  |  | Signature of Authorized Officer<br>G. COUSINS-VAN STEEN           |

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9300444  
SA 70724

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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